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Dissociation Dynamics of $ClONO_2$ and Relative Cl and ClO Product Yields following Photoexcitation at 308 nm

Teresa A. Moore and Mitchio Okumura*

Arthur Amos Noyes Laboratory of Chemical Physics,† California Institute of Technology, Pasadena, California 91125, USA

Masahito Tagawa‡

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109, USA

Timothy K. Minton*

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109 and Center for Biofilm Engineering and Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, USA

Chlorine nitrate photolysis at 308 nm has been investigated with a molecular beam technique. Two primary decomposition pathways, leading to $Cl + NO_3$ and $ClO + NO_2$, were observed. The branching ratio between these two respective channels was determined to be $0.67 \pm 0.06 : 0.33 \pm 0.06$. This ratio is an upper limit because some of the ClO photoproducts may have undergone secondary photodissociation. The angular distributions of the photoproducts with respect to the direction of polarization of the exciting light were anisotropic. The anisotropy parameters were $\beta = 0.5 \pm 0.2$ for the $Cl + NO_3$ channel and $\beta = 1.1 \pm 0.2$ for the $ClO + NO_2$ channel, indicating that dissociation of $ClONO_2$ by either pathway occurs within a rotational period. Weak signal at mass-to-charge ratios of 35 and 51, arising from products with laboratory velocities close to the beam velocity, was observed. While this signal could result from statistical dissociation channels with a total relative yield of 0.07 or less, it is more likely attributable to products from ClO secondary photodissociation or from dissociation of clusters.

Chlorine nitrate ($ClONO_2$) plays a key role in stratospheric chemistry as a reservoir for reactive chlorine and nitrogen oxides.[1,2] Photolysis is a major decomposition process for $ClONO_2$,[3] and has been the subject of many studies.[4–13] At wavelengths <250 nm, photodecomposition follows two primary channels:[9]

$$ClONO_2 + h\nu \rightarrow ClO + NO_2; \qquad \Delta H = 26 \text{ kcal mol}^{-1} \tag{1}$$

$$\rightarrow Cl + NO_3; \qquad \Delta H = 40 \text{ kcal mol}^{-1} \tag{2}$$

† Contribution no. 9024.

‡ Visiting scientist from Department of Precision Engineering, Faculty of Engineering, Osaka University, 2-1 Yamada-oka, Suita, Osaka 565, Japan.

Channel (2) can lead directly to loss of two ozone molecules *via* the following reactions:[13]

$$NO_3 + h\nu \rightarrow NO + O_2 \quad (3a)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (3b)$$

$$Cl + O_3 \rightarrow ClO + O_2. \quad (3c)$$

Toumi *et al.* have recently shown in model studies that this catalytic cycle[13] including steps (2) and (3*a*)–(3*c*) becomes the dominant ozone-loss mechanism in the latter stages of springtime Arctic ozone depletion.[14] In this model, the extent of ozone loss depends upon the quantum yield of channel (2), especially at $\lambda > 300$ nm. Toumi *et al.* used the value of 0.9 for this quantum yield, which was recommended by the 1992 JPL evaluation of kinetic data.[15] However, results from our laboratory at shorter wavelengths (193 and 248 nm) showed the $Cl + NO_3$ product yield to be significantly lower,[9] a conclusion later corroborated by other groups.[10–12] A lower yield at longer wavelengths would diminish the predicted contribution of the $ClONO_2$ catalytic cycle to Arctic ozone depletion and reduce the predicted magnitude and duration of the ozone-loss episode.

Sander and co-workers have recently obtained evidence from flow tube studies that excited $ClONO_2$ formed by wavelengths >300 nm lives long enough to be quenched under stratospheric conditions.[12] Quenching of $ClONO_2$ photolysis would profoundly affect the partitioning of the Cl and NO_x budgets and would largely eliminate the $ClON_2$ catalytic cycle as a candidate loss mechanism for stratospheric ozone. In their experiment, Sander and co-workers observed products from channels (1) and (2) when $ClONO_2$ was excited by a broadband Xe lamp; however, at wavelengths >300 nm they found that the total quantum yield was significantly quenched at N_2 buffer gas pressures >50 Torr. Under their conditions (*ca.* 50 Torr and 200 K), the mean time between gas-kinetic collisions is 3 ns, so an excited molecule must have a lifetime of the order of nanoseconds or longer to be quenched rather than dissociated.

Previous flow-tube studies revealed no direct evidence of a relatively long-lived state following UV excitation of $ClONO_2$.[4,8,10,11] However, recent *ab initio* calculations by Graña *et al.* do predict the existence of a metastable state.[16] These authors performed high-level configuration interaction (CI) and coupled-cluster calculations to predict the vertical excitation energies and oscillator strengths for transitions to eight singlet and eight triplet states of $ClONO_2$ between 400 and 160 nm. They also found a bound, metastable triplet state, with a non-planar geometry, lying 62 kcal mol^{-1} above the ground-state equilibrium configuration. If $ClONO_2$ were formed in this state either by direct excitation or by relaxation from an initially prepared state, the excited $ClONO_2$ could conceivably persist for nanoseconds or longer.

The fate of chlorine nitrate excited at wavelengths >300 nm has important implications for stratospheric ozone depletion. To address questions concerning the dissociation pathways and the possibility of a long-lived excited state, we extended our previous photodissociation studies of $ClONO_2$ to a longer wavelength. With the use of molecular beam methods, we can directly detect photoproducts, measure their relative yields, and determine angular and translational energy distributions in the absence of collisions. Furthermore, we can infer the timescale for dissociation from the anisotropy of the product angular distribution. In our earlier experiments, we observed comparable yields of Cl and ClO products from $ClONO_2$ photolysis at both 193 and 248 nm.[9] We calibrated the relative detector sensitivity for Cl and ClO by performing an experiment on Cl_2O photolysis at 308 nm and found Cl : ClO branching ratios of 0.57 : 0.43 and 0.67 : 0.33 for $ClONO_2$ photolysis at 248 and 193 nm, respectively. Furthermore, we observed anisotropic angular distributions for the two channels and inferred that the dissociation is prompt, occurring within a rotational period ($\tau_{rot} \approx 9$ ps at the rotational

temperature of the beam). Here we present results from a similar investigation of $ClONO_2$ photolysis at 308 nm.

Experimental

The molecular beam apparatus and methods have been described in detail elsewhere.[9,17] Briefly, a molecular beam was crossed with a laser beam in a low-pressure region at the centre of rotation of a rotatable mass spectrometer detector[18] (Fig. 1). Collisionless conditions allowed for detection of primary dissociation products recoiling away from the beam direction. Centre-of-mass (cm) product translational energy and angular distributions were derived from the arrival-time distributions of the neutral photoproducts over a calibrated flight length as a function of detector angle away from the beam direction.

Continuous molecular beams were formed by passing H_2 over $ClONO_2$ at $-50\,^{\circ}C$ or He over Cl_2O at $-74\,^{\circ}C$ and expanding the mixture through a 0.1 mm diameter quartz nozzle maintained at $+5\,^{\circ}C$. $ClONO_2$ was seeded in hydrogen rather than helium in order to obtain a faster beam, which enhanced the signal through kinematic focussing. Stagnation pressures of the gas mixtures were 300 Torr for the $ClONO_2$ experiment and 200 Torr for the Cl_2O experiment. The $ClONO_2$ data were obtained in two sets, with corresponding beam velocities of 1350 and 1580 m s^{-1}, as determined by beam time-of-flight (TOF) distributions taken with the aid of a chopper wheel. The Cl_2O beam velocity (1480 m s^{-1}) was determined by examining the arrival time of the laser-induced depletion of signal at a mass-to-charge ratio (m/z) of 37 with the detector directly viewing the molecular beam.[19,20]

Cl_2O was synthesized by oxidation of Cl_2 on HgO and was purified by pumping on the sample at $-118\,^{\circ}C$ (ethanol slush bath).[21] $ClONO_2$ was synthesized from the reaction of Cl_2O with N_2O_5 and purified first by cannulation and then by pumping on the sample at $-95\,^{\circ}C$ (methanol slush bath).[22] Purity was checked by a survey of beam TOF distributions at all masses where signal was observed. The only impurities in either

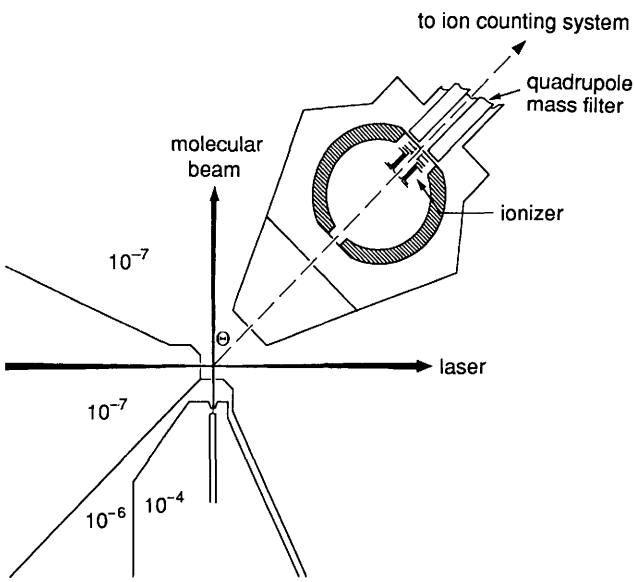

Fig. 1 Schematic diagram of the molecular beam photodissociation experiment. The numbers correspond to pressures in Torr for the various regions. Θ is the detector angle.

molecular beam could be attributed to dimers and/or clusters. A small peak in the beam TOF at $m/z = 146$ ($ClONO_2 \cdot NO_2^+$) indicated that clusters were present in the $ClONO_2$ beam; however, the product signals observed were insensitive to the relative magnitudes of the cluster signals.

The molecular beam was crossed in the interaction region with a laser beam at 308 nm from a Lambda Physik EMG103 excimer laser operating at 200 Hz. The laser beam was randomly polarized in a plane perpendicular to the scattering plane and parallel to the molecular beam axis. The laser beam was focussed to a spot size of 2.5 mm × 2.5 mm, where it intersected the molecular beam. The laser pulse energy used for the $ClONO_2$ experiment was 170 mJ. The consequent laser fluence was high enough that secondary photodissociation of the primary ClO products was a concern; however, the low absorption cross-section[15] of $ClONO_2$ at 308 nm ($\sigma = 1.6 \times 10^{-20}$ cm^2) required the use of relatively high laser fluences to make the primary photoproduct signals observable. For the Cl_2O experiment, a pulse energy of 126 mJ was used for data collection at $m/z = 51$, and the laser was attenuated with a stack of quartz plates to 36 mJ per pulse for data collection at $m/z = 35$ in order to minimize secondary photodissociation of the ClO product. TOF distributions were collected at $m/z = 35$ (Cl^+), 51 (ClO^+), 30 (NO^+), 46 (NO_2^+), 16 (O^+) and 81 ($ClONO^+$), and angular distributions of product signals detected at $m/z = 35$, 51 and 46 were measured.

Results and Analysis

Analysis of TOF and angular distributions was carried out by a forward convolution technique.[20,23–25] For each channel, trial cm translational energy $P(E_T)$ and angular $\omega(\theta)$ distributions were transformed to the laboratory frame of reference to obtain a predicted number density TOF distribution $N(t)$ that could be compared with the experimental data. The $P(E_T)$ and $\omega(\theta)$ distributions were then adjusted iteratively until the predicted TOF distributions agreed with the observed distributions at all angles.

The data were similar to our earlier results at 193 and 248 nm.[9] A single peak was prominent at $m/z = 51$ (see Figs. 2 and 3), which we assigned to ClO from the ClO + NO_2 channel by analogy with our previous results. The $m/z = 35$ TOF distribution contained two main components, the slower of which matched the peak at $m/z = 51$, indicating that it must arise from fragmentation of ClO to Cl^+ in the ionizer.† We assigned the fast component at $m/z = 35$ to Cl from the Cl + NO_3 channel. We used the TOF spectra taken at $m/z = 35$ and 51 to derive the cm translational energy distributions for the two dissociation channels (Fig. 4).

We verified our assignments of the two dissociation channels by using the $P(E_T)$ and $\omega(\theta)$ distributions derived from the ClO^+ and Cl^+ data to predict the TOF distributions for the respective counterfragments, NO_2 and NO_3 (Fig. 5). No signal was observed at $m/z = 62$, the NO_3 parent mass, but the TOF spectrum collected at $m/z = 46$ (NO_2^+) fitted well with the distribution predicted for the NO_3 fragment by the $P(E_T)$ and $\omega(\theta)$ distributions for the Cl + NO_3 channel. Apparently, the NO_2^+ signal comes not from NO_2, but from NO_3 which fragments to NO_2^+ in the ionizer. The bimodal TOF distribution at $m/z = 30$ (NO^+) could not be fit from the $P(E_T)$ and $\omega(\theta)$ distributions for either the Cl + NO_3 or ClO + NO_2 channels alone, but it could be fit with a sum of contributions from the predicted TOF distributions for both NO_3 and NO_2 fragments. Hence, both NO_3 and NO_2 photofragments lead to NO^+ in the ionizer; similar ionizer fragmentation patterns were observed in our previous study.[9] The ability to fit both counterfragments of each dissociation channel with the use of the same $P(E_T)$ and $\omega(\theta)$

† The 4 μs difference in peak positions of the ClO signals detected at $m/z = 51$ and $m/z = 35$ reflects the mass dependence of the ion flight time from the ionizer of the mass spectrometer to the Daly-type ion counter. The ion flight time was determined to be $t = 3.5\,(m/z)^{1/2}$ μs.

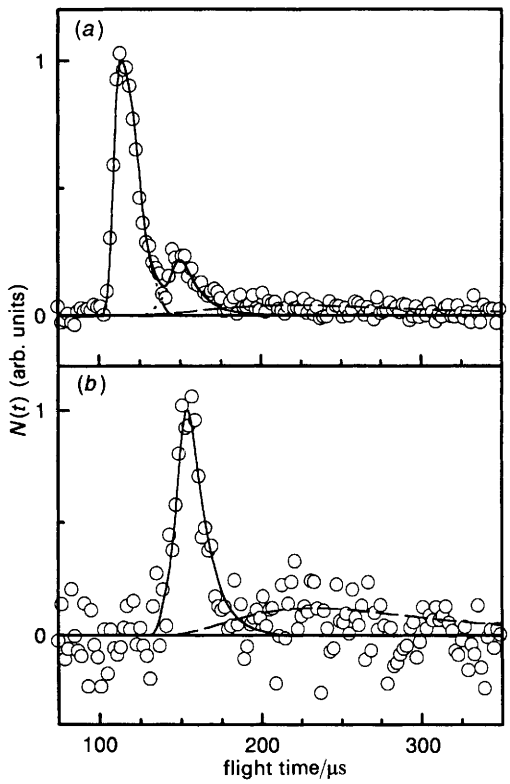

Fig. 2 TOF distributions $N(t)$ collected at a detector angle of 30° for (*a*) Cl^+ and (*b*) ClO^+ fragments. The molecular beam velocity was 1580 m s^{-1}. Fits to the dominant product channels, $Cl + NO_3$ and $ClO + NO_2$, are calculated with optimized centre-of-mass translational energy $P(E_T)$ and angular $\omega(\theta)$ distributions (see Fig. 4 and 6). The long-dashed line at slow times in (*b*) is a hypothetical fit based on the assumption that ground electronic state ClO and NO_2 products are formed by a statistical (RRKM) process. The long-dashed line at slow times in (*a*) is also a hypothetical fit based on statistical (RRKM) decay that leads to ground electronic state products. This 'fit' includes contributions to a Cl^+ signal from both $ClO + NO_2$ and $Cl + NO_3$ channels. The upper limit on the total yield from both channels is determined from the fits in (*a*) to be 0.07. (*a*) (·—·) $Cl + NO_3$, (·····) $ClO + NO_2$; (*b*) (——) $ClO + NO_2$.

distributions thus confirms our original assignments of the two primary photodissociation channels.

Laboratory angular distributions of ClO, Cl and NO_3 were obtained from the integrated TOF data detected at $m/z = 51$, 35 and 46, respectively. At $m/z = 51$ and 46, where the TOF distributions corresponded only to a single photoproduct, the signal for each detector angle was simply integrated. The Cl angular distribution was extracted from the $m/z = 35$ TOF distributions by integrating the calculated TOF distributions for the Cl^+ signal arising from the $Cl + NO_3$ channel [obtained from the optimized $P(E_T)$ and $\omega(\theta)$ distributions].

The cm angular distribution must have the form $\omega(\theta) \propto 1 + \beta P_2(\cos\theta)$, where P_2 denotes the second-order Legendre polynomial and θ the angle between the electric field vector of the excitation photon and the product recoil direction in the cm reference frame.[23,26] β is the anisotropy parameter and must lie in the range $-1 \leqslant \beta \leqslant 2$. We obtained $\beta = 1.1 \pm 0.2$ for the $ClO + NO_2$ channel from the ClO angular distribution and $\beta = 0.5 \pm 0.2$ for the $Cl + NO_3$ channel from both the Cl and NO_3 angular distributions. The fits used to determine the anisotropy parameters are shown in Fig. 6.

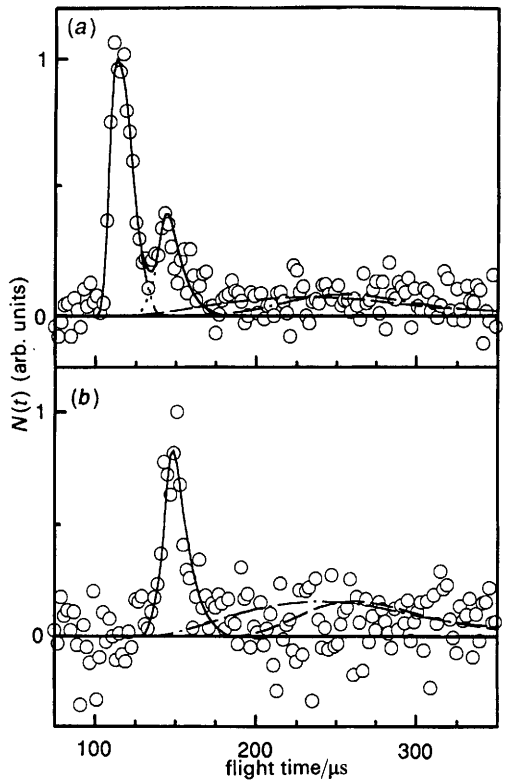

Fig. 3 TOF distributions collected at a detector angle of 15° for (*a*) Cl^+ and (*b*) ClO^+ fragments. The molecular beam velocity was 1350 m s^{-1}. Fits to the main peaks are calculated with the same $P(E_T)$ and $\omega(\theta)$ distributions used to achieve the analogous fits in Fig. 2. Two kinds of hypothetical fits are shown at longer flight times. One is based on the assumption of statistical decay to ground-state products and the other is based on the assumption of statistical decay to excited-state products. As in Fig. 2, the hypothetical fits at $m/z = 35$ include dissociation along both $ClO + NO_2$ and $Cl + NO_3$ product channels. Statistical decay to excited state products *via* channels (4) and (5) leads to low product translational energies and thus a smaller possible contribution to the signal than dissociation to ground-state products. The upper limit on the total yield of ground-state products is 0.07, while the upper limit on the total yield of excited-state products at this detector angle is 0.03. The total yield of all slow products cannot exceed 0.07. At detector angles of 30° and larger, the excited-state products cannot be detected because their centre-of-mass velocities are too low. (*a*) (·—·) $Cl + NO_3$, (···) $ClO + NO_2$, (—·—) RRKM (ground-state products), (— — —) RRKM (excited-state products); (*b*) (——) $ClO + NO_2$, (—·—) RRKM (ground-state products), (— —) RRKM (excited-state products).

The broad, slow signal at $m/z = 35$ may be explained by a number of possible mechanisms: spontaneous secondary dissociation, dissociation of clusters formed in the beam expansion, secondary photodissociation of primary ClO photoproducts, or a third primary channel leading to products with low cm translational energies. We can rule out spontaneous secondary dissociation because the $P(E_T)$ distribution [Fig. 4(*b*)] implies that no ClO photoproducts have enough internal energy to dissociate. Clusters were present in the beam, but we expect the contribution from dissociation of clusters to the $m/z = 35$ TOF to be small because changes in the stagnation pressure did not significantly alter the magnitude of the slow signal relative to the fast peaks. The most likely explanation for the tail at $m/z = 35$ is secondary photodissociation of ClO. The ClO absorption cross-section is larger than that of $ClONO_2$ at 308 nm, and at the high laser

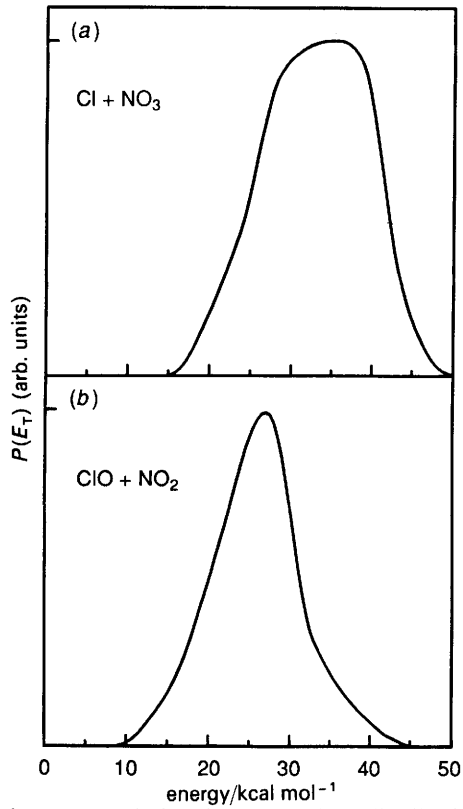

Fig. 4 Optimized centre-of-mass translational energy $P(E_T)$ distributions for the two dominant photodissociation channels. For the Cl + NO_3 channel, $\langle E_T \rangle$ = 32.9 kcal mol^{-1}, which is 62% of E_{avail}. For the ClO + NO_2 channel, $\langle E_T \rangle$ = 26.0 kcal mol^{-1}, which is 39% of E_{avail}.

fluences used, some secondary photodissociation of ClO is expected. However, we could not model the secondary photodissociation, because the signal-to-noise ratio was too low. We therefore could not eliminate the possibility of a third primary dissociation channel forming products with low translational energies.

Direct dissociation on a triplet surface to ClONO + $O(^3P)$ could conceivably contribute to a slow signal at m/z = 51 and 35 through fragmentation to ClO^+ or Cl^+ in the ionizer. ClONO might also fragment to NO_2^+ or NO^+ and give rise to a slow signal at m/z = 46 and 30. The energy available for translation after breaking the O—N bond is only *ca.* 26 kcal mol^{-1}, and the ClONO fragment will recoil slowly from the relatively light O-atom counterfragment. Therefore, the minimum flight time possible at a detector angle of 30° is 133 μs (not including ion flight time), and any signal present should manifest itself as a peak in the slow tail of the product TOF distributions. The only TOF distributions which showed an obvious hint of slow signal were the Cl^+ distributions. If all slow signal at m/z = 35 not assigned to the dominant channels did come from ClONO, then the ClONO + O yield would be *ca.* 0.07. Even this small yield is suspect because (1) no photofragment signal was detected at the ClONO parent mass (m/z = 81), (2) no obvious slow signal was seen at other masses and (3) ClONO can only be formed by a spin-forbidden process at an excitation wavelength of 308 nm.

Statistical dissociation of $ClONO_2$ could also lead to products with low translational energies. The cm translational energy distributions for products of a statistical dissociation process have a maximum near zero and decay rapidly with E_T; therefore,

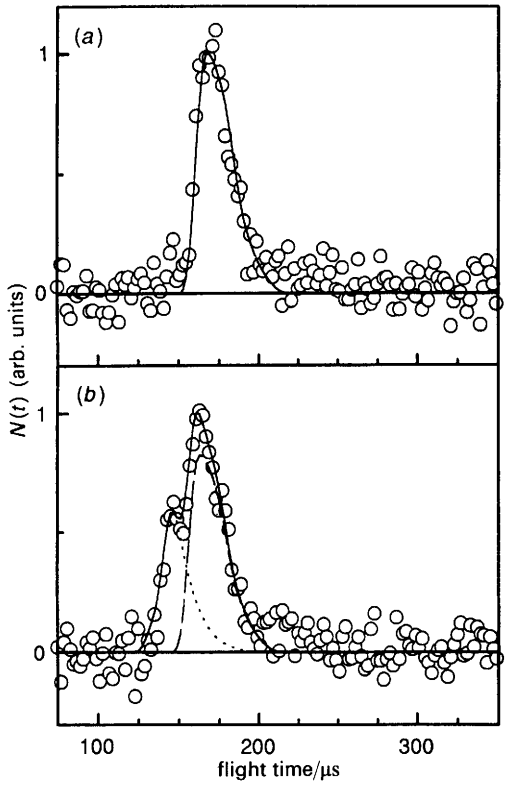

Fig. 5 TOF distributions collected at 30° for (*a*) NO_2^+ and (*b*) NO^+ fragments. The peak in (*a*) is fitted with the $P(E_T)$ and $\omega(\theta)$ distributions for the $Cl + NO_3$ channel under the assumption that all the signal at $m/z = 46$ arises from NO_3 which fragments to NO_2^+ in the ionizer. The bimodal distribution in (*b*) apparently contains signal from both NO_3 and NO_2 products which fragment to NO^+ in the ionizer; this distribution is fitted with two components corresponding to both $Cl + NO_3$ (— —) and $ClO + NO_2$ (– – –) channels.

the observed signal would have low cm velocities. At the smallest detector angle used here, 15°, we can detect Cl products from the $Cl + NO_3$ channel with total cm translational energies $E_T \geqslant 0.7$ kcal mol^{-1} and ClO products from the $ClO + NO_2$ channel with $E_T \geqslant 1.4$ kcal mol^{-1}. The experiment should therefore be sensitive to statistical dissociation channels with available energies of a few kcal mol^{-1} above threshold.

We can estimate the maximum possible yield from statistical dissociation by fitting the slow component to a statistical model, but the modeling will depend upon the final dissociation channel. Several dissociation channels are energetically available to $ClONO_2$ with 92.8 kcal mol^{-1} of internal energy (*i.e.* the photon energy of 308 nm light). While statistical dissociation of $ClONO_2$ on the ground electronic state potential-energy surface will lead predominantly to ClO and NO_2 in their ground electronic states, an excited state of $ClONO_2$ may correlate to a higher energy asymptote and dissociate to form excited-state products. The statistical decay rate will be slower and the translational energy release smaller for channels with lower available energy. We therefore considered dissociation *via* two excited-state channels which consume most of the 308 nm photon energy:

$$ClONO_2 \rightarrow Cl(^2P) + NO_3(\tilde{A}\,^2E'); \qquad \Delta H = 83 \text{ kcal mol}^{-1} \tag{4}$$

$$\rightarrow ClO(a\,^4\Sigma^-) + NO_2(\tilde{X}\,^2A_1); \qquad \Delta H \approx 77 \text{ kcal mol}^{-1} \tag{5}$$

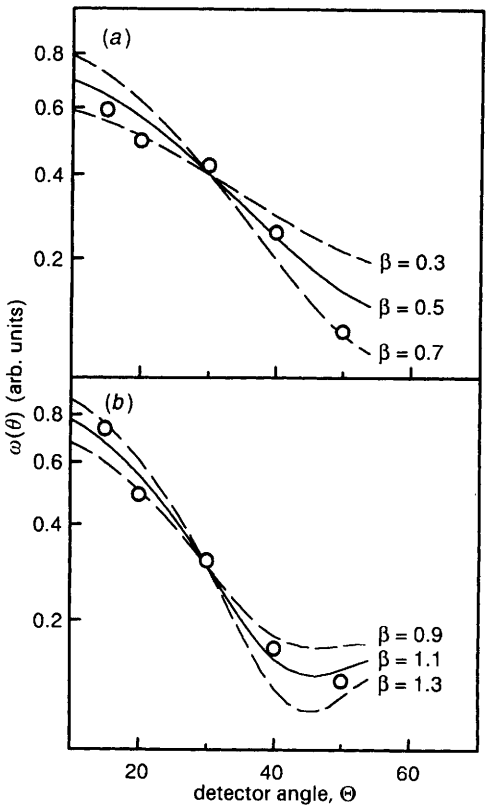

Fig. 6 Semi-logarithmic plot of the laboratory angular distributions for the two photodissociation channels observed: (*a*) Cl + NO_3, (*b*) ClO + NO_2. The circles are the experimental data, and the lines are the calculated distributions using values of the anisotropy parameter β shown. The solid lines are the best fit to the data; the dashed lines are calculated using upper and lower limits for the parameter β.

We proposed the existence of a bound ClO quartet state in a previous study of photoproducts from Cl_2O dissociation,[17] and this hypothesis was confirmed theoretically by Langhoff, who computed the energy and geometry of this state.[27] In order to estimate the maximum possible yield of these channels, we first performed RRKM calculations to obtain a cm translational energy distribution for each channel.[28] We then compared the slow component of the TOF distribution at the relevant m/z to the TOF distribution predicted by the RRKM $P(E_T)$ distribution. We obtained upper limits on the yields by assuming that the signal in the slow components arose solely from statistical dissociation (see Fig. 2 and 3). We estimated a yield of 0.05 for dissociation to ground-state ClO and NO_2 products, based on the signal at $m/z = 51$. We then determined the ClO contribution to the slow component at $m/z = 35$ by using the same ClO ionizer fragmentation pattern observed for the main peaks. We assumed that the remainder of the slow signal at $m/z = 35$ corresponded to Cl products from statistical decay to ground-state Cl and NO_3 products and obtained a maximum yield of 0.02 for this channel. Thus, the maximum total relative yield for statistical dissociation to ground-state products *via* either channel is 0.07. For the excited-state products, we found a maximum possible total yield of 0.03 based on the data collected at 15° (Fig. 3). However, the RRKM $P(E_T)$ distributions for the excited-state product channels predict negligible contributions to the slow signal at larger detector angles, because the $P(E_T)$ distributions fall

off quickly with E_T. Our inability to achieve a consistent fit of all the data under the assumption of excited-state products makes it highly unlikely that channels (4) or (5) play any role in $ClONO_2$ photodissociation at 308 nm. In any case, these yields are upper limits because it is improbable that all of the slow signal arises from statistical dissociation. Secondary photodissociation, observed unambiguously in our previous experiments at shorter wavelengths, may even account for all of this broad underlying signal at $m/z = 35$. Regardless of the actual product channel assumed, we conclude that any statistical dissociation process is at most a minor channel.

We performed a photodissociation experiment on Cl_2O at 308 nm in order to calibrate the relative detection efficiency for Cl and ClO and thereby determine the branching ratio between the two channels in the photodissociation of $ClONO_2$. The Cl_2O data (not shown) were analogous to previous observations and were fit with the same $P(E_T)$ and $\omega(\theta)$ distributions as before.[17] The relative yields for the two photodissociation channels of $ClONO_2$ following excitation at 308 nm were determined to be 0.67 ± 0.06 for the $Cl + NO_3$ channel and 0.33 ± 0.06 for the $ClO + NO_2$ channel. Our results may underestimate the ClO yield because the primary ClO product has a significant probability of undergoing secondary photodissociation during the laser pulse; therefore the Cl : ClO branching ratio of 0.67 : 0.33 is an upper limit.

Discussion

Excited-state Lifetime

The anisotropy of the angular distributions allows us to determine whether the main products associated with the dominant peaks were formed by prompt dissociation, *i.e.* occurring in less than a rotational period, τ_{rot}. If the excited molecule has time to rotate before dissociating, then the molecule will change orientation, causing the angular distribution to become more isotropic. Rotational averaging thus reduces the absolute magnitude of β, though not necessarily exactly to zero. We can estimate upper limits on the minimum values of β for the two channels with the use of expressions that Yang and Bersohn have derived for calculating β when the dissociating molecule is long-lived.[29] We assume (1) that the transition dipole moments are parallel to the axes of the respective dissociating bonds, (2) that the geometry of $ClONO_2$ does not change on going to the dissociative state and (3) that $ClONO_2$ can be approximated as a symmetric top ($\kappa = -0.89$). We find that the upper limits on the anisotropy parameters for a long-lived state of $ClONO_2$ are $\beta = 0.07$ for dissociation to $ClO + NO_2$ and $\beta = 0.13$ for dissociation to $Cl + NO_3$. Effects such as vibrational averaging and breakdown of the symmetric-top assumption will reduce β further. The calculated values lie below the uncertainties in the anisotropy parameters for the two main channels, $\beta = 1.1 \pm 0.2$ for $ClO + NO_2$ and $\beta = 0.5 \pm 0.2$ for $Cl + NO_3$. The observed anisotropies thus indicate that dissociation *via* either channel occurs within τ_{rot}. Assuming a typical rotational temperature of *ca.* 50 K in the molecular beam, τ_{rot} would be *ca.* 9 ps. We conclude that the main products observed in this experiment are formed in $\lesssim 9$ ps, which is shorter than the mean collision time (*ca.* 5 ns) under stratospheric conditions, and thus cannot arise from a long-lived excited state.

We could not rule out assignment of the slow signal at $m/z = 35$ and 51 to a third dissociation channel, such as statistical decomposition, with low cm translational energies; however, the contribution from such a process will be small. Dissociation *via* a statistical process should be dominated by fission of the weakest bond, making ground state ClO and NO_2 the most likely major products if $ClONO_2$ dissociates on its ground electronic state surface. We derived an upper limit of 0.05 for the yield of this channel from the $m/z = 51$ data (Fig. 1 and 2). However, the RRKM lifetime for ground-state $ClONO_2$ with 92.8 kcal mol^{-1} of internal energy will be on the subpicosecond time-

scale. To account for a nanosecond lifetime, we would have to invoke a rate-limiting step, such as internal conversion or intersystem crossing from an initially prepared state. Statistical dissociation of metastable $ClONO_2$ could occur on a nanosecond timescale only if the available energy is small (on the order of 10 kcal mol^{-1} or less for $ClONO_2$), *e.g.* dissociation to a channel near threshold leading to excited-state products. Dissociation to channels (4) and (5) may have lifetimes as long as nanoseconds, but we did not have enough information to calculate accurate decay rates for processes so close to threshold. The bound triplet state predicted by Graña *et al.* is a candidate for this metastable state, but there is no information on its possible decomposition pathways. Although the translational energy release would be even lower than for dissociation to ground-state products, our experiment still places an upper limit of 0.03 on the total relative yield for the plausible product channels (4) and (5) near 93 kcal mol^{-1} (see Fig. 2). Thus, the slow product signal could account for only a small fraction of the total observed products; furthermore, all of these estimates are upper bounds, because secondary photodissociation of ClO will likely contribute substantially to the observed slow signal at $m/z = 35$.

Given our beam velocity, laser spot size and the solid angle viewed by our detector, we can only detect fragments from excited $ClONO_2$ molecules that dissociate within 2.5 μs. Our sensitivity allows us to detect molecules in states with dissociation lifetimes $\tau \leqslant 10$ μs; metastable states which live longer would go unobserved in our experiment. Such lifetimes are significantly longer than typical mean collision times of 1–10 ns in flow tube experiments, where unit quantum yields are observed for $ClONO_2$ photolysis at buffer gas pressures of 5–10 Torr.[7,10,11] If dissociation occurs through a state with a lifetime of 10 μs or longer, then the metastable $ClONO_2$ must undergo $>10^3$ gas kinetic collisions without being quenched at these pressures. Thus, the molecular beam and flow tube studies are together consistent with a long-lived metastable only if that state has a lifetime $\tau > 10$ μs and is very inefficiently quenched.

Our results would also be consistent with the experiment of Sander and co-workers if a metastable state of $ClONO_2$ is prepared by excitation at wavelengths >308 nm. Sander and co-workers photolysed chlorine nitrate with a broad-band, filtered Xe lamp whose output extended from *ca.* 300 nm to visible wavelengths.[12] Such long-wavelength radiation would be absorbed in the 370–380 nm region, where Molina and Molina[3] observed a weak absorption band that was distinct from absorption bands deeper in the ultraviolet. This band lies close to 362 nm, the wavelength that Graña *et al.* predict for the lowest vertical triplet excitation.[16] This state is predicted to be directly dissociative, but may lead by curve crossing to the bound metastable state. Additional experiments at longer wavelengths are necessary to examine the possiblility that this band involves a transition leading to formation of a long-lived state; however, the small absorption cross-section, nine times lower at 362 nm than at 308 nm, will make these measurements difficult.

Product Yields

We found channels (1) and (2) to dominate $ClONO_2$ photochemistry at 308 nm; the total yield of all other possible channels must be $\leqslant 0.07$. The Cl : ClO product branching ratio was determined to be 0.67 : 0.33. The relative yield of 0.33 for ClO is a lower limit, because some of the ClO products may have undergone secondary photodissociation. This branching ratio does not agree with a number of earlier studies performed at $\lambda > 300$ nm by Smith *et al.*,[4] Chang *et al.*,[13] Knauth and Schindler[6] and Margitan.[7] The last three experiments all found near unit quantum yields of Cl atoms and failed to detect ClO products, even for photolysis at wavelengths <300 nm. The JPL evaluation,[15] which recommends quantum yields of 0.9 ± 0.1 for the $Cl + NO_3$ channel and 0.0 for the $ClO + NO_2$ channel, was based primarily on the results of the most direct

study, that of Margitan. However, our results are more consistent with recent unpublished flow-tube studies[10–12] which detect both channels with similar relative yields.

The decreased yield for dissociation of the weakest bond, $ClO—NO_2$, in the present study relative to our earlier results suggests that photons at 308 nm excite transitions favouring fission of the Cl—O bond. Graña *et al.* calculate that the lowest singlet state $1\,^1A''$ possesses ClO $n \rightarrow \sigma^*$ character and has a vertical excitation wavelength of 284 nm with an oscillator strength *ca.* 1% of the band strength at 190 nm. The next highest state, the $2\,^1A''$ state, is predicted to be a $\pi \rightarrow \pi^*$ transition localized on the NO_2 group at 252 nm but with zero oscillator strength. While excitation to the $1\,^1A''$ state could explain the higher Cl yield at 308 nm relative to 248 nm, it is not consistent with the observed angular distributions which are indicative of a parallel transition. To excite a state of A″ symmetry, the transition moment must be out of plane and perpendicular to either dissociation coordinate in the ground-state geometry. A perpendicular transition would result in a negative value of β unless the dissociating bond rotates significantly out of plane prior to dissociation. There are many states of both symmetries at slightly higher energies, and excitation at 308 nm could instead readily excite the Franck–Condon wing of a dissociative A′ state. It is possible that there are simultaneous parallel and perpendicular transitions to multiple excited states or a transition to a mixed state with the dipole transition moment aligned midway between the two bond axes, making the net β small and positive. The complexity of the $ClONO_2$ excited-state manifold suggests that photodissociation of $ClONO_2$ cannot be described by a simple bond-selective picture but rather that curve crossings and the dynamics of nuclear motion following excitation may largely determine the final product branching ratio.

The dominance of direct dissociation processes at excitation wavelengths as long as 308 nm implies that it is important to consider a catalytic cycle involving $ClONO_2$ photolysis in models of stratospheric ozone depletion. However, our finding of a significant yield for the $ClO + NO_2$ channel will lead to a decrease in the ozone-depleting efficiency of the $ClONO_2$ cycle from what has been predicted. At mid-latitudes, where this cycle contributes only 3–5% of the ozone loss,[2] the new product yield ratio will not affect the predicted ozone depletion. The impact will be greater on model predictions of ozone loss in the Arctic polar spring as well as in the Antarctic collar region, where Toumi *et al.* have shown that this cycle plays a major role.[14]

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